Intensified one-step biodiesel production from high water and free fatty acid waste cooking oils

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Abstract

Homogenous alkali-catalysed biodiesel production from waste cooking oil (WCO) requires acid-catalysed pre-treatment steps due to high free fatty acid (FFA) contents. This study investigated strategies to obtain high yields of fatty acid methyl esters (FAME) from one-step base-catalysed transesterification of WCO containing high levels of free fatty acids (up to 5.5wt%) and 3wt% of water by altering operating conditions. About 98% FAME yield in homogeneous $NaOCH_3$-catalysed transesterification was obtained within 5min reaction time at methanol to WCO molar ratios of 12:1 – 18:1 and 3wt% catalyst loading for WCO containing 1.53% FFA and 0.12wt% water. It was found that high molar ratios of methanol to oil (> 6:1) could prevent saponification. At 5.5wt% FFA and 3wt% water contents, ≥96.5% FAME yield was achieved at 18:1 molar ratio of methanol to WCO within 5mins compared to only 62.8 ± 1.2% for a molar ratio of 6:1. Mathematical modelling (MATLAB) was used to predict FAME yields at various conditions and validated using experimental data. Sets of conditions identified in this study can be used to rapidly produce biodiesel from low quality triglyceride sources in a single step base-catalysed process.

Keywords: Waste cooking oil, base catalysis, free fatty acids, water content, mathematical model, saponification.

1. Introduction

Biodiesel is a mixture of fatty acid alkyl esters (≥96.5% according EN14214) which is used as a renewable alternative to petro-diesel. This accounts for about 82% of the biofuels production in the EU [1]. Biodiesel is usually produced via transesterification of triglyceride-containing feedstock (vegetable oils, animal fat etc.) with short chain alcohols, such as methanol, ethanol, propanol or butanol [2]. The most commonly used alcohol is methanol due to its low prices and availability, producing a mixture of fatty acid methyl esters as shown in Fig. 1.

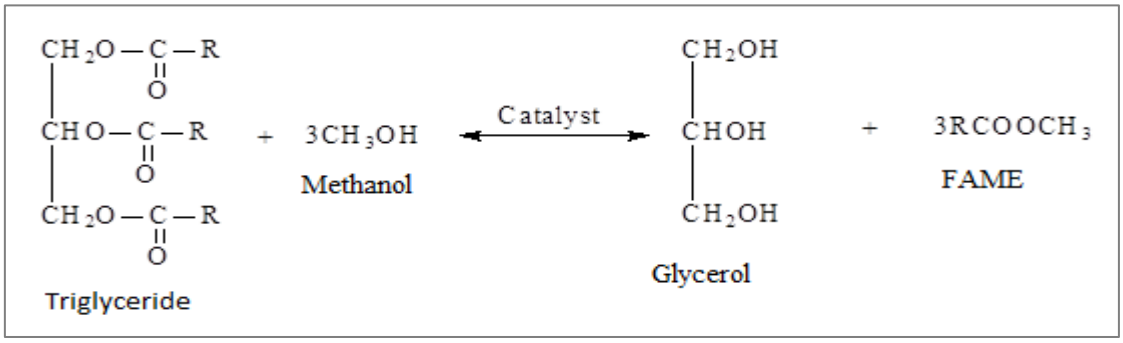

Fig. 1: Triglyceride transesterification reaction

Generally, biodiesel production reactions are catalysed using base catalysts [3-6], acid catalysts [7-9], and biocatalysts or enzymes [10-12]. Non-catalytic processes such as supercritical fluid processing can also be used for biodiesel production [13-15]. The biocatalysts and supercritical fluid processes are not commonly used because of their high operating costs. Supercritical methanolysis of oils is not cost-effective due to the high pressure (~8 MPa) and temperature (~ 350˚C) required for the reaction [13], whereas the enzyme-catalysed biodiesel process remains too expensive to be used for any meaningful

industrial application because of the high cost of enzymes, slow reaction rates, and deactivation of the enzymes [12]. Consequently, developments in catalysis of biodiesel production reactions have mainly focused on acid and base catalysts.

Base-catalysed homogeneous transesterification is the most commonly used process in conventional biodiesel production. This process uses base catalysts such as alkali metal hydroxides and methoxides (NaOH, KOH, $NaOCH_3$, $KOCH_3$), particularly sodium methoxide which accounts for than 60% of the commercial biodiesel plants [6]. The use of alkaline catalysts is preferred because of the higher reaction rate of these catalysts, typically about 4000 times faster than acid catalysts at moderate temperatures [16]. A major disadvantage of base catalysts for biodiesel production is that pre-treatment steps are required if low quality feedstock, such as WCO which may contain high FFAs ≥ 0.5wt% and water ≥ 0.3wt%, is used [9, 17]. This is due to the saponification of triglycerides and FAME [18], leading to emulsification and difficulties in the products separation [19]. Therefore, either an acid-catalysed transesterification, or a two-step process requiring acid-catalysed pre-treatment becomes necessary for biodiesel production from feedstocks with high FFA and water. In both cases, esterification of the FFA (Fig. 2) occurs in the presence of the acid catalyst.

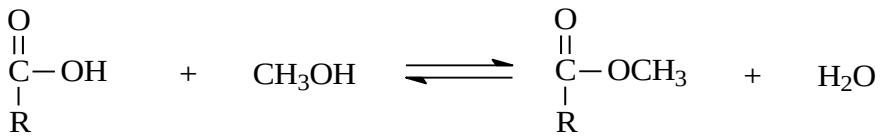

Fig. 2: Free fatty acid esterification

A number of acid catalysts such as sulphuric acid, phosphoric acid, hydrochloric acid and organic sulphonic acids have been investigated for catalysis of biodiesel production reactions [4, 20, 21]. Among these acid catalysts, the sulphuric and organic sulphonic

acids are the most widely used, especially H_2SO_4 because of its higher activity, low price and availability [22, 23]. One of the challenges of acid catalysts is that long reaction times and high temperatures are required for the acid-catalysed transesterification. It has been reported that approximately 20h are required to achieve high FAME yield (99%) in a homogeneous acid-catalysed transesterification of soybean oil with methanol at 120˚C using H_2SO_4 catalyst [24]. Another disadvantage of the acid-catalysed homogeneous biodiesel process is that all the equipment has to withstand the corrosive effect of the acids. The cost of corrosion resistant vessels significantly increases the capital cost of acid-catalysed process.

Notwithstanding these problems, acid catalysts are widely used for catalysis of triglyceride transesterification with methanol [25-29], even at moderate FFA (< 4wt %) and water (≤ 0.2wt %) contents [26, 29]. Acid-catalysed processes were used to achieve 99% FAME yield after 4h reaction time, in a transesterification of waste frying oil containing 6wt% FFA, at 70°C, 169–190kPa pressure and 1:245:3.8 molar ratio of oil:methanol:H_2SO_4 catalyst [27]. In another study, about 95.1% FAME conversion was obtained after 150min reaction time, using an acid-catalysed (cucurbituril-protected $Cs_{2.5}H_{0.5}PW_{12}O_{40}$) transesterification of WCO that contained 2.5wt% FFA, at reported optimum conditions of 2wt% catalyst, 70°C and 11:1 methanol to WCO molar ratio [26]. The long reaction time and higher operating temperature required by the acid catalysts adds to the costs of biodiesel production even when using cheaply available WCO feedstock.

Due to the low rates of acid-catalysed processing of biodiesel, a two-step process involving acid-catalysed esterification of the FFA, followed by base-catalysed

transesterification has been proposed [29, 30]. This method was used to process Chinese oil (3.06wt% FFA) and trap grease (57.02wt% FFA), via esterification at 75°C and 45min for the oil, 75°C and 13h for the grease, and followed by transesterification of the pre-treated oil and grease at 6:1 methanol to oil (grease) molar ratio, 1.2wt% KOH and 65°C, to achieve approximately 91.7% FAME yield after 19min reaction time [29]. A two-step process, involving esterification of a waste fryer grease containing 5.6wt% FFA and 0.2wt% water at 3:1 molar ratio, 2wt% H_2SO_4 catalyst and 50°C for about 5h, and followed by transesterification at 6:1 molar ratio, 50°C and 60min reaction time, was used to achieve >90% FAME yield [30]. The use of an acid-catalysed FFA esterification step and base catalyst for the transesterification step reduces the overall reaction time compared to one-step acid catalysis. However, the overall reaction time remains longer than the base-catalysed process. This leads to a substantial additional energy cost which negates the savings on WCO feedstock when producing biodiesel using two-step process.

Although biodiesel production using WCO could reduce the overall product cost, as the feedstock can contribute up to 60-70% total cost [31, 32], the complex treatment steps and long reaction times could reduce its benefits. There is an urgent need to develop a simple biodiesel process that would allow for utilisation of vast amounts of low quality WCO feedstocks for biodiesel production. For instance, over 250 million litres of used cooking oil was collected in the UK in 2011 [33]. A study on the characteristics of restaurant waste oil has shown that the FFA contents vary from 0.17wt% to 6.52wt%, whereas the water contents were less than 0.2wt% [34]. The FFA contents of WCO in most other studies were less than 6wt% [28, 30, 32, 35]. Therefore, substantial amount of the available WCO contain low FFA and water contents, and could be processed at reaction conditions similar to the conventional biodiesel process without any

modification. This has been demonstrated in an existing study where an alkali-catalysed transesterification was used to achieve 98% biodiesel yield after 20 – 40min using waste frying oil containing 0.5wt% FFA and 0.08wt% water, at reaction conditions of 5:1 methanol to oil molar ratio, 0.83wt% KOH and 50°C temperature [35].

However, the base-catalysed system is decreasingly effective as the FFA content of the WCO increases. It has been reported that a maximum FAME yield of 89.8% was obtained for transesterification of WCO that contained 3.63wt% FFA at reaction conditions of 6:1 methanol to oil molar ratio, 1wt% NaOH, 50°C and 90min [30]. Another study also showed that only about 50% FAME yield could be achieved in a transesterification of waste fryer grease containing 5.6wt% FFA and 0.2wt% water at reaction conditions of 6:1 methanol to grease molar ratio, 1wt% KOH catalyst and 30min reaction time [28]. These studies at higher FFA contents (>3wt %) demonstrated that the base-catalysed transesterification at the conventional reaction conditions would not be adequate in achieving an acceptable levels of FAME conversions from WCO. At these FFA and water contents of WCO, it becomes difficult to apply transesterification conditions commonly used for virgin vegetable oils, i.e. methanol to oil molar ratio of 6:1-9:1 and 1-1.5%wt base catalysts [3, 18, 34, 36-39]. The alkali catalysts used in the conventional process become ineffective due to soap formation and deactivation, leading to low FAME yields [17, 18, 38, 40-42]. To ensure that biodiesel is produced from WCO at a competitive market price, a suitable alkali-catalysed processing strategy must be developed to allow for high FAME conversions at these conditions, considering that most of the available WCO have $\leq$ 6wt% FFA and $\leq$ 0.2wt% water contents. A robust alkali-catalysed process could be developed based on numerical modelling of the kinetics of the transesterification and other side reactions that occur during biodiesel production [18].

1.1 Reactions in base-catalysed transesterification of WCO

There is a general agreement among researchers that the triglyceride transesterification shown in Fig. 1 occurs via three consecutive step-wise reversible reactions [36, 43, 44]. These reactions are presented in Eqs. (1) – (3).

$$TG + MA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} FAME + DG \quad (1)$$

$$DG + MA \underset{k_4}{\overset{k_3}{\rightleftharpoons}} FAME + MG \quad (2)$$

$$MG + MA \underset{k_6}{\overset{k_5}{\rightleftharpoons}} FAME + GL \quad (3)$$

(MA: methanol; TG: triglyceride; DG: diglyceride; MG: monoglyceride; GL: glycerol)

Apart from the triglyceride transesterifications, there are a number of side reactions which determine the extent of the overall FAME conversions [18, 45]. During transesterification in alkali-catalysed process, the TG and FAME molecules in the reaction mixture could be saponified by the metal hydroxide ions to from soap as shown in Eqs. (4) and (5). The reaction in Eq. (4) is expected to proceed via three consecutive step-wise irreversible reactions, from TG to DG and soap, DG to MG and soap, and finally from MG to soap and GL. However, only the overall rate constant (k_7) has been determined [18].

$$TG + 3OH^- \xrightarrow{k_7} 3Soap + GL \quad (4)$$

$$FAME + OH^- \xrightarrow{k_8} Soap + MA \quad (5)$$

Another major side reaction which occurs in alkali-catalysed transesterification of WCO is FFA neutralisation. The FFA in the WCO could react with both hydroxide and methoxide ions to form soap [46], as shown in Eq.(6).

$$FFA + OH^-(RO^-) \xrightarrow{k_9} Soap + H_2O(ROH) \quad (6)$$

The rates of the transesterification and the side reactions are affected by the quality of the feedstock, principally by its FFA and water contents. The presence of water in the alkali-catalysed transesterification process determines the relative amounts of methoxide (CH_3O^-) available for transesterification, and the hydroxide ions (OH^-) that cause saponification reactions. The relative availability of the CH_3O^- and OH^- is controlled by an equilibrium [47, 48] shown in Eq. (7).

$$CH_3OH + OH^- \underset{k_y}{\overset{k_x}{\rightleftharpoons}} CH_3O^- + H_2O \quad (7)$$

$$K_{eq} = \frac{k_x}{k_y}$$

A kinetic model derived by combining the reactions in Eqs. (1) – (7) has been developed to allow for numerical simulations of the alkali-catalysed transesterification. The rate expressions for various chemical species obtained by combinations of the above reactions are described in Eqs. (8) – (18).

$$r_{CH_3O^-} = \frac{d[CH_3O^-]}{dt} = k_x[MA][OH^-] - k_y[H_2O][CH_3O^-] - k_9[FFA][CH_3O^-] \quad (8)$$

$$r_{OH^-} = \frac{d[OH^-]}{dt} = k_y[H_2O][CH_3O^-] - k_x[MA][OH^-] - k_9[FFA][OH^-] \ldots$$
$$-k_7[TG][OH^-] - k_8[FAME][OH^-] \quad (9)$$

$$r_{TG} = \frac{d[TG]}{dt} = [CH_3O^-](-k_1[TG][MA] + k_2[DG][FAME]) - k_7[TG][OH^-] \quad (10)$$

$$r_{DG} = \frac{d[DG]}{dt} = [CH_3O^-](k_1[TG][MA] + k_4[MG][FAME] - k_2[DG][FAME] \ldots$$
$$- k_3[DG][MA]) \quad (11)$$

$$r_{MG} = \frac{d[MG]}{dt} = [CH_3O^-](k_3[DG][MA] + k_6[GL][FAME] - k_4[MG][FAME] \ldots$$
$$- k_5[MG][MA]) \quad (12)$$

$$r_{FAME} = \frac{d[FAME]}{dt} = [CH_3O^-](k_1[TG][MA] + k_3[DG][MA] + k_5[MG][MA] \ldots$$
$$-k_2[DG][FAME] - k_4[MG][FAME] - k_6[GL][FAME]) - k_8[FAME][OH^-] \quad (13)$$

$$r_{MA} = \frac{d[MA]}{dt} = [CH_3O^-](k_2[DG][FAME] + k_4[MG][FAME] + k_6[GL][FAME] \ldots$$
$$+ k_y[H_2O] - k_1[TG][MA] - k_3[DG][MA] - k_5[MG][MA]) \ldots$$
$$+ k_8[FAME][OH^-] - k_x[MA][OH^-] \quad (14)$$

$$r_{GL} = \frac{d[GL]}{dt} = [CH_3O^-](k_5[MG][MA] - k_6[GL][FAME]) + k_7[TG][OH^-] \quad (15)$$

$$r_{Soap} = \frac{d[Soap]}{dt} = [OH^-](k_7[TG] + k_8[FAME] + k_9[FFA]) \quad (16)$$

$$r_{FFA} = \frac{d[FFA]}{dt} = -k_9([FFA][OH^-] + [FFA][CH_3O^-]) \quad (17)$$

$$r_{H_2O} = \frac{d[H_2O]}{dt} = k_x[MA][OH^-] - k_y[H_2O][CH_3O^-] + k_9[FFA][OH^-] \quad (18)$$

The aim of this study was to identify strategies for simple biodiesel production from WCO using base catalysis, when using WCO that contains high FFA and water. Development of such a simple biodiesel process would substantially reduce biodiesel market price, improve global biodiesel consumption, especially in rural areas, and consequently lead to significant reduction in hazardous emissions associated with petro-diesel combustion. This study used a combination of experimental investigations and MATLAB numerical simulations of kinetic model for the base-catalysed biodiesel process which was developed by the authors [18]. The rate expressions in Eqs. (8) – (18) were numerically modelled in MATLAB 7.12.0 (R2011a) using ODE45 solver (Runge-Kutta method).

Table 1: Rate constants used in modelling

Rate constant (L. mol^{-1}.min^{-1})	Reactions	References
$k_1 = 4.260\ x\ 10^9\ e^{-\frac{58{,}740}{RT}}$	TG $\longrightarrow$ DG	[18]
$k_2 = 4.304\ x\ 10^6\ e^{-\frac{44{,}930}{RT}}$	DG $\longrightarrow$ TG	[18]
$k_3 = 2.176\ x\ 10^{11}\ e^{-\frac{67{,}146}{RT}}$	DG $\longrightarrow$ MG	[18]
$k_4 = 6.559\ x\ 10^9\ e^{-\frac{58{,}184}{RT}}$	MG $\longrightarrow$ DG	[18]
$k_5 = 8.679\ x\ 10^5\ e^{-\frac{30{,}010}{RT}}$	MG $\longrightarrow$ GL	[18]
$k_6 = 1.975\ x\ 10^7\ e^{-\frac{46{,}009}{RT}}$	GL $\longrightarrow$ MG	[18]
$k_7 = 1.269\ x\ 10^{11}\ e^{-\frac{69104}{RT}}$	RSO $\longrightarrow$ Soap	[18]
$k_8 = 1.962\ x\ 10^{10}\ e^{-\frac{61{,}160}{RT}}$	FAME $\longrightarrow$ Soap	[45]
$k_9 = 6.136\ x\ 10^5\ e^{-\frac{31{,}394}{RT}}$	FFA $\longrightarrow$ Soap	[46]
$K_{eq} = \frac{k_x}{k_y} = 3.2$ (79.5 (mol.L^{-1})	$OH^- \rightleftharpoons CH_3O^-$	[47, 48]

The MATLAB models were applied to predict the effects of catalyst concentrations, methanol molar ratio, FFA and water contents on transesterification of WCO, and these were validated using experimental data. The initial rate constants (Table 1) for the numerical modelling were obtained from previous work [18], and these values were adjusted to obtain the line of best fit (< 5% error) to the experimental data. The rate constants that fitted the experimental data were 0.2 times lower than those in the Table 1. The experimental and numerical modelling approach were combined to identify the reaction conditions necessary for high FAME conversions from the WCO at high FFA (up to 5.5wt %) and water (up to 3wt %).

2.0. Experimental methods

2.1. Materials

Anhydrous methanol (99.8% purity), acetic acid (99% purity), heptane (99% purity), methyl heptadecanoate (99.0% purity) and methyl oleate (99.0% purity) were purchased from Sigma-Aldrich, whilst the sodium methoxide (30wt% $NaOCH_3$ in methanol) was obtained from Alfa Aesar. The waste cooking oil used in the study were kindly provided by a Chinese Restaurant in Newcastle upon Tyne, UK.

2.2. Characterisation of the waste cooking oil

The following properties of the WCO were analysed using ASTM and AOCS standard testing procedures: density (ASTM D1298), FFA (AOCS Cd 3d-63) and water contents (AOCS Ca 2e-84). The fatty acids profile of the WCO was determined through gas chromatograph (GC) analysis of fatty acid methyl esters produced via alkali-catalysed transesterification and acid-catalysed esterification/transesterification of the WCO with methanol.

2.3. Transesterification of WCO with methanol using $NaOCH_3$ catalyst.

The experiments were carried out using a 100mL two-neck glass reactor assisted with a magnetic stirrer, which connect with a condenser and a thermocouple for monitoring the reaction temperatures. The required volume of WCO (40mL for reaction mixture at 6:1 methanol to WCO molar ratio) was heated in the batch reactor to 60°C, followed by the addition of proportionate amount of methanol/$NaOCH_3$ solution (10mL) which had been pre-heated to the reaction temperature. The reaction mixture was mixed vigorously using a magnetic stirrer at 600 rpm to ensure that the reaction was mass transfer independent [18, 44, 49]. All the experiments were carried out at a fixed temperature of 60°C. The effect of operating parameters such as molar ratios of methanol to WCO (6:1- 18:1), catalyst concentrations (0.6wt% -3wt% based on the WCO), reaction times (0.5min to 60min), FFA content (1.53 – 5.5wt%) and water contents (0.12wt% to 3wt%) were investigated. The experiments with WCO containing >1.53wt% FFA and > 0.12wt% water were performed using WCO that was spiked with oleic acid and water. In all the experiments, approximately 1mL samples were collected at various reaction times, typically 0.5, 2, 5, 8, 10, 15, 20, 30, 40, 50 and 60min, and quenched with appropriate amounts (50µL) of acetic acid. The biodiesel layers were removed after phase separation, and dried in an oven at 110°C for 2h to remove excess methanol, acetic acid and water. These samples were stored in 2mL sealed vials and later analysed using the GC. The experimental data were used to validate the results from MATLAB numerical simulations from our existing kinetic model [18].

2.4. Analysis

The FAME contents of the samples were determined using a 5890 Hewlett Packard Series II GC, equipped with a BPX70 CP wax capillary column of 30m length, 0.25µm film

thickness and 0.32mm internal diameter. The temperature of the column was initially held at 150°C for 1min, ramped to 210°C at a heating rate of at 10°C/min and held for 10min (17min total run time). The GC injector and FID detector temperatures were set at 250 and 260°C, respectively. Amounts of FAME in the samples were quantified using a 10mg/mL of methyl heptadecanoate internal standard prepared in heptane, in accordance with the British standards (BS EN 14103: 2003). The FAME yield was determined using Eq. (19).

$$\text{FAME yield (\%)} = \frac{FAME\ content\ in\ the\ sample}{Maximum\ theoretical\ FAME} * 100 \quad (19)$$

3. Results and Discussion

3.1. Properties of the waste cooking oil

The calculated molecular weight of the WCO was 877.8 g/mol based on the fatty acid profile presented in the Table 2. As illustrated in Table 2, six major fatty acid methyl esters: palmitic, stearic, oleic, linoleic, linolenic, and icosenoic were identified and quantified using the methyl heptadecanoate internal standard, similar to the profile of rapeseed oil (RSO). The WCO contained 1.53% FFA, 1153ppm water, and had density of 924 $kg.m^{-3}$. The FFA concentration was much higher than the conventional limit for conventional base-catalysed homogeneous transesterification (FFA ≥ 0.5wt %), whereas the water content was within the tolerable range (water ≥ 0.3wt %) for biodiesel production using base catalysts [9, 17].

Table 2: Fatty acid profile of the WCO compared with that of vegetable oil

Fatty acids	Molar weight (g/mol)	% fatty acid of WCO and virgin RSO		
		WCO (this study)	RSO (this study)	Ref. [50]
Palmitic (C16:0)	256.4	6.1	5.3	4.3
Stearic (C18:0)	284.5	1.8	1.7	-
Oleic (C18:1)	282.5	64.2	63.2	64.7
Linoleic (C18:2)	280.5	19.4	19.8	16.5
Linolenic (C18:3)	278.4	8.4	8.6	9.4
Icosenoic (C20:1)	310.5	-	1.4	-

3.2 Numerical model for biodiesel production using alkali catalysts

Fig. 3 shows that with 1.53wt% FFA and 0.12wt% water in WCO, homogeneous alkali-catalysed biodiesel production had a lower FAME yield at 6:1 methanol to WCO molar ratio than at 12: 1 or 18:1. The maximum FAME yields at the 6:1 molar ratio and catalyst concentrations of 3wt% and 1.8% were approximately 93% after about 2min and 5min reaction times, respectively. A further increase in the reaction time at 6:1 molar ratio decreased FAME yield, e.g. from maximum yields of 93% to 81% at 3wt% catalyst, and to 88% at 1.8wt%. For the reaction at 6:1 molar ratio and 0.6wt% catalyst, the FAME yield continued to increase with time, reaching 86% at 60min reaction time. The slow reaction rate at this condition was due to some of the $NaOCH_3$ being consumed via neutralisation with FFA.

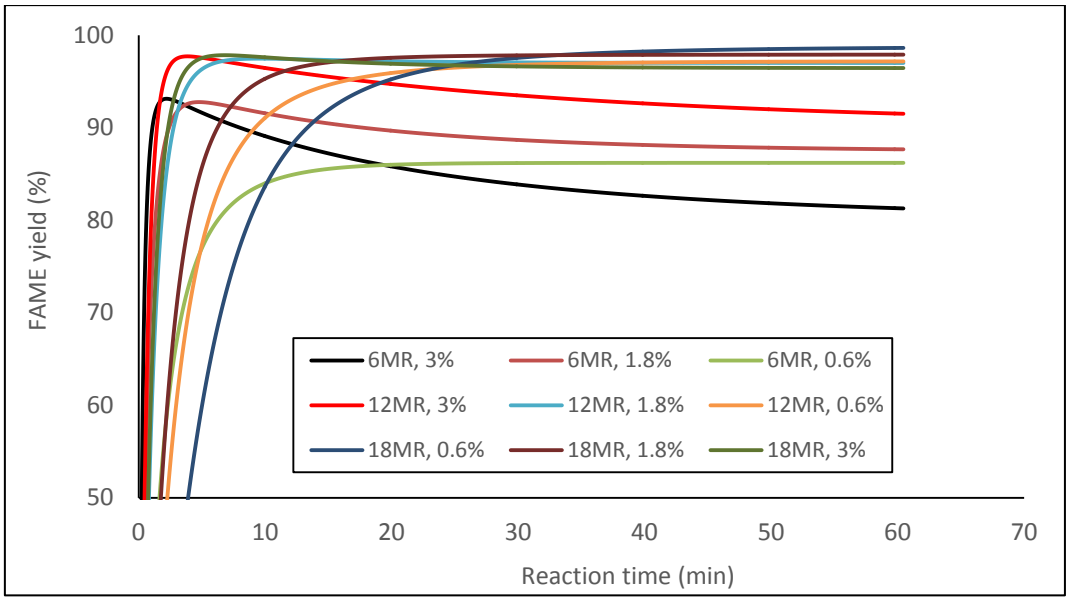

Fig. 3: Numerical models for WCO conversions to FAME at 60°C temperature for reactions at methanol to WCO molar ratios (MR) of 6:1 – 18:1, 1.53wt% FFA, 0.12wt% water and $NaOCH_3$ catalyst in the range of 3wt% - 0.6wt%.

A gradual reduction in FAME yield with further increase in the reaction time at 6:1 molar ratio and 3 – 1.8%wt was attributed to increased rates of FAME saponification at high catalyst content. There is an equilibrium between the $NaOCH_3$ catalyst and the water in the WCO feedstock, which produces NaOH as shown in Eq. (20), below. The increased NaOH concentration in the reaction mixture leads to saponification of both triglycerides and FAME.

$$NaOCH_3 + H_2O \leftrightarrow CH_3OH + NaOH \qquad (20)$$

Clearly, a higher molar ratio of methanol is required to shift the equilibrium reaction towards $NaOCH_3$ formation. Therefore, an increase in the methanol molar ratio had a substantial positive effect on the FAME conversion. The predicted maximum FAME yield increased from 93% at 6:1 methanol to WCO molar ratio, to about 98% at 12:1 and 18:1 molar ratios for 3wt% $NaOCH_3$. The effects of hydroxide on FAME saponification

reactions were less pronounced when increasing molar ratios of methanol to WCO. Around 6% reduction in FAME yield was observed at 12:1 molar ratio, but only 1.5% at 18:1 molar ratio after 60mins. At low catalyst concentration (0.6wt %), the FAME conversions were >97% at 12:1 and 18:1 molar ratios without any evidence of FAME saponification. It was found that the reaction rates for the WCO transesterification were slower than that of virgin rapeseed, probably due to interference by some other impurities in the WCO. Consequently, the reaction rate constants were about 0.2 times lower than that reported for virgin rapeseed oil in Table 1 [18]. The observed low reaction rate for the WCO was consistent with other studies [32, 51].

3.3. Validations of the numerical model for the transesterification of WCO.

The experimental validations of the numerical model for WCO transesterification at 6:1 – 18:1 methanol to oil molar ratio, 0.6 – 3wt% $NaOCH_3$ catalyst, 0.12wt% water, 1.53wt% FFA and 60°C are shown below in Fig. 4. The FAME conversions predicted by the model agreed well with the experimental data (R^2 = 0.95 – 0.99). At a 6:1 molar ratio (Fig. 4(a)), the maximum FAME yield decreased from 92.8 ± 2.3% at 2min reaction time to 80.0 ± 1.1% after 60min for 3wt% catalyst, and from 93.5 ± 2.1% at 15min reaction time to 86.0 ± 1.5% after 60min for 1.8wt% catalyst. These are comparable with the simulation results. A small decrease in FAME yield (1.5 - 6%) was also observed at 3wt% catalyst and higher molar ratios of methanol to WCO, with reductions in the maximum FAME yields from 98.1 ± 2.0% to 91.1 ± 3.0 at 12:1 molar ratio (Fig. 4 (b)), and from 98.0 ± 1.3% to 97.6 ± 2.4 at 18:1 molar ratio (Fig. 4(c)).

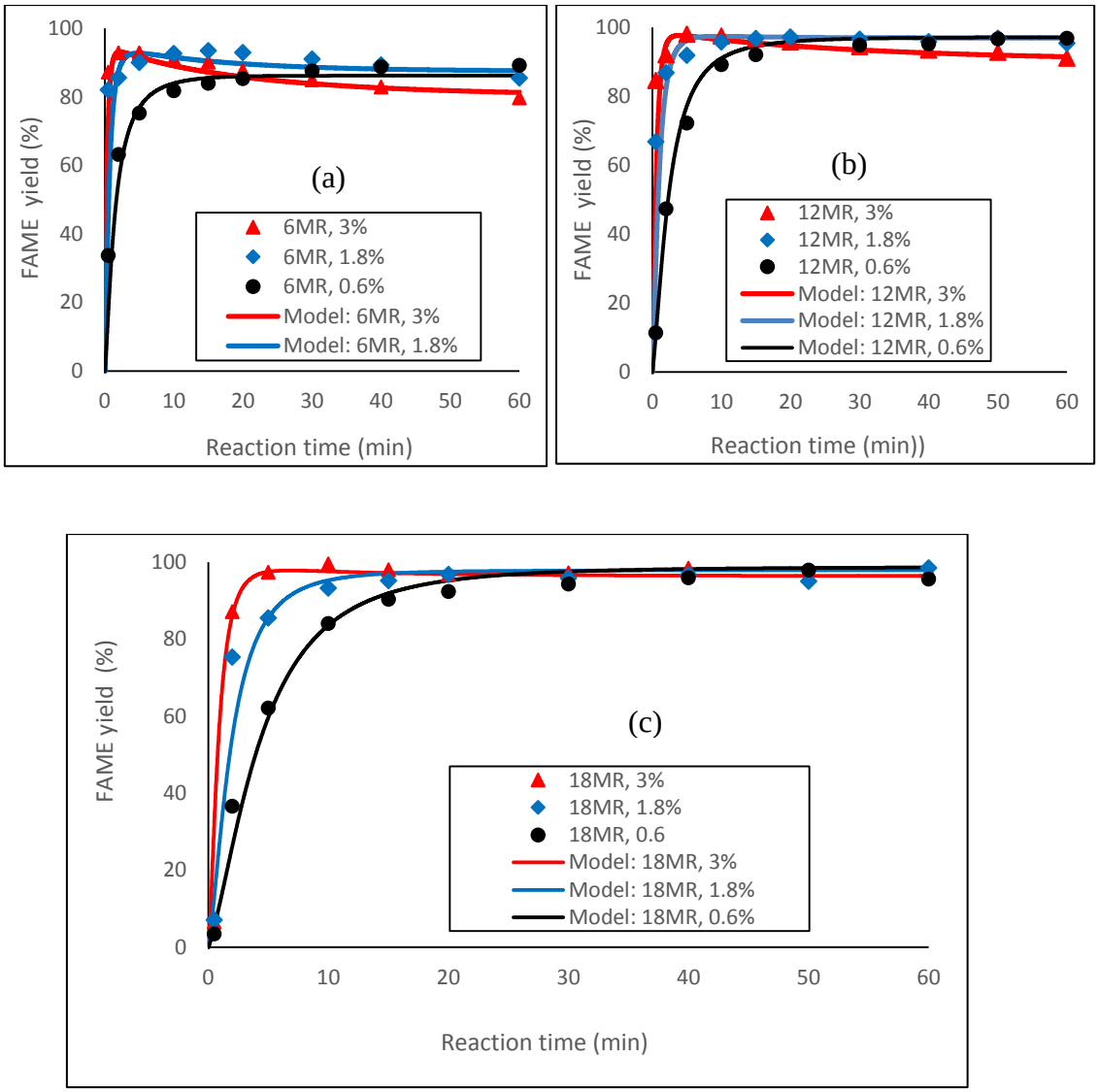

Fig. 4: Experimental and numerical models for conversions of WCO to FAME at 60°C temperature and 600rpm stirrer mixing intensity for reactions at 6:1 - 18:1 methanol to WCO molar ratio, 1.53wt% FFA, 0.12wt% water and 0.6wt% - 3wt% $NaOCH_3$ catalyst.

Fig. 4 shows that at low catalyst concentration, i.e. 0.6wt%, WCO transesterification occurred at a slower rate, requiring nearly 60min reaction time to achieve acceptable FAME yields (≥96.5%) both at 12:1 and 18:1 molar ratios. At a 6:1 molar ratio, catalyst concentration of 0.6wt% was not sufficient to catalyse the WCO transesterification, only 89.2 ± 2.1% FAME yield was achieved after 60min reaction time. This was attributed to the removal of substantial amount of the catalyst by the FFA in the WCO. Further

investigations of the operating parameters for the WCO transesterification with methanol at higher FFA levels and water are discussed in the section 3.4.

3.4 Biodiesel production from WCO containing high FFA and water contents

The FAME yields for transesterifications of WCO containing 0.12wt% - 3wt% water and 1.53wt% - 5.5wt% FFA at methanol to WCO molar ratios of 6:1 and 12:1 are shown in Fig. 5. Maximum FAME yields of about 93% were achieved after 2min at 6:1 molar ratio (Fig. (5a)), and 98% after 5min at 12:1 molar ratio (Fig. (5b)) at the lowest FFA (1.53wt %) and water (0.12wt %) contents.

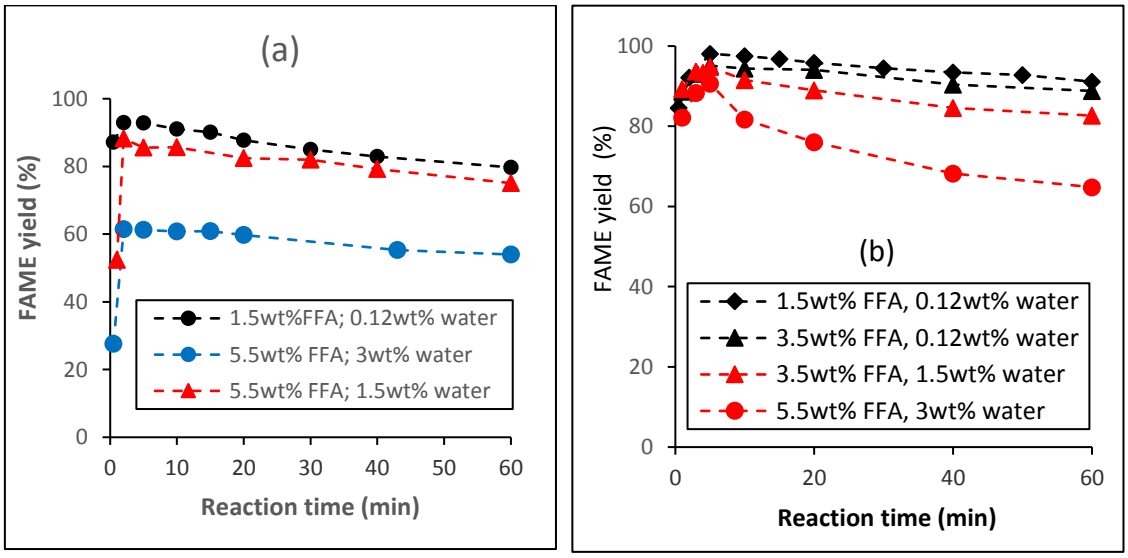

Fig. 5: FAME yield at 60°C temperature3wt% $NaOCH_3$ and 600rpm mixing speed for reactions: (a) methanol to WCO molar ratio of 6:1, water contents of 0.12wt% - 3wt% and FFA levels of 1.5wt% - 5.5wt%; (b) methanol to WCO molar ratio of 12:1, water contents of 0.12wt% - 3wt% and FFA levels of 1.5wt% - 5.5wt%.

As predicted by the model, an increase in FFA and water increased FAME saponification reaction rates, thereby reducing FAME yields as previously reported [18]. Fig. 5 clearly

shows that at the highest FFA (5.5wt%) and water (3wt%) contents investigated, the maximum FAME yields obtained were 62.8 ± 1.2% at 2min for a 6:1 molar ratio (Fig. 5(a)), and 90.7 ± 1.0% at 5min for 12:1 molar ratio (Fig. 5(b)). These conditions exhibited the steepest slope following the maximum, as the rate of saponification was highest at these conditions, as would be expected. The FAME yield, after 5min at 12:1 molar ratio using WCO with 5.5wt% FFA and 3wt% water contents, was similar to that reported for a two-step process on a waste fryer grease containing 5.6wt% FFA and 0.2wt% water content, where esterification of the waste fryer grease for 5h, followed by transesterification at 6:1 molar ratio for 60min are required to achieve >90% FAME yield [28]. Only 50% FAME yield was achieved after 30min for transesterification of the waste fryer grease at 6:1 molar ratio, 1wt% KOH and 50°C temperature [28]. It can be concluded that a methanol to oil molar ratio of 6:1, which is commonly used in conventional biodiesel production, was not sufficient to convert high FFA and water containing feedstock to FAME, due to high rates of triglyceride and FAME saponification. Increasing the reaction time after the maximum FAME was achieved, resulted in a reduction in FAME yield. This is due to saponification of FAME by the metal hydroxide produced by the equilibrium reactions of $NaOCH_3$ and water. The FAME saponification is shown in Eq. (21). The methoxide-hydroxide equilibrium in Eq. (20) indicates that higher methanol molar ratio was required to reduce the amounts of metal hydroxide produced. This is consistent with the results in Fig. 5, which shows that high molar ratio of methanol slows down the saponification process.

$$RCOOCH_3 + NaOH \leftrightarrow RCOONa + H_2O \quad (21)$$

Results of the investigations on the effects of FFA and water contents of the WCO at higher methanol molar ratio (18:1) are shown in Fig. 6.

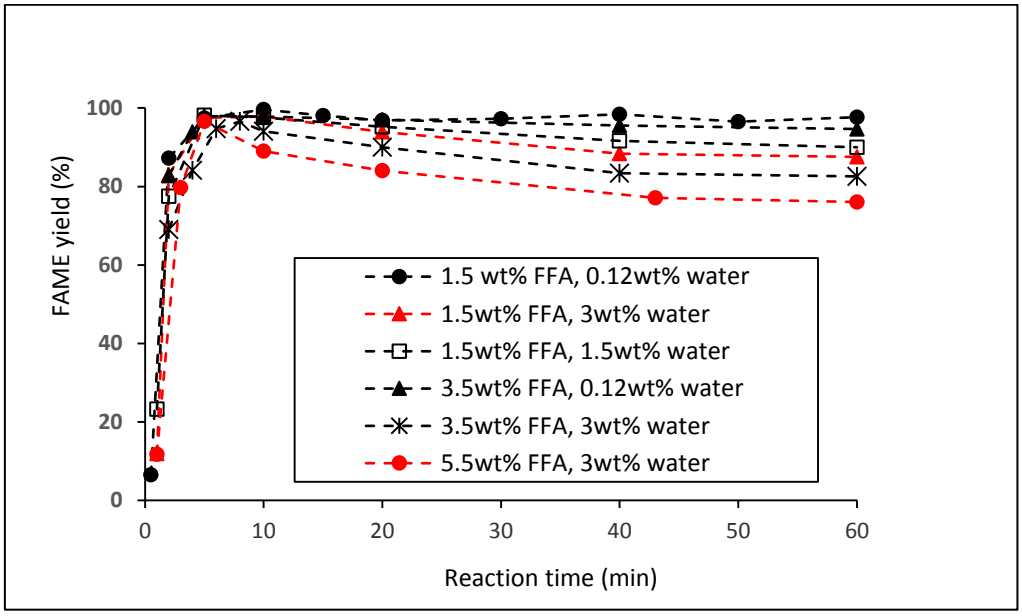

Fig. 6: FAME yields at 60°C temperature, 3wt% $NaOCH_3$ and 600rpm mixing speed for transesterification at 18:1 methanol to WCO molar ratio, 0.12wt% - 3wt% water content and FFA levels of 1.5wt% - 5.5wt% based on WCO.

The maximum FAME yields increased from, 62.8 ± 1.2% at 2min for 6:1 methanol to WCO molar ratio in Fig. 5(a), and 90.7 ± 1.0% at 12:1 molar ratio in Fig. 5(b), to 96.6 ± 1.4% at 5min for 18:1 molar ratio, for transesterification of WCO containing 5.5wt% FFA and 3wt% water, as shown in Fig. 6. An increase in the reaction time at 18:1 molar ratio led to rapid decrease in the WCO conversions to FAME from the maximum value to about 76.0 ± 1.0% after 60min. It can be clearly observed that maximum FAME yield (≥96.5%) was achieved at 18:1 molar ratio after 5min reaction time at these FFA and water contents. The experimental and simulated FAME yields after 5min reaction for transesterification at 18:1 molar ratio and 3wt% $NaOCH_3$ catalyst were similar (R^2 >0.95), with or without addition of FFA and water as shown in Fig. 6. Both the experimental and model results showed that the FAME yield decreased from the maximum value of about 97% to approximately 76.0% after 60min reaction time at 5.5wt% FFA and 3wt% water

contents. For industrial-scale biodiesel production using a stirred tank reactor, 5min reaction time may not be enough due to non- uniform mixing leading to mass and heat transfer constraints. However, this process can be implemented in an intensified reactor such as oscillatory baffled reactors, where uniform effective mixing can be maintained [38], allowing ≥96.5% FAME yield to be achieved within 5min.

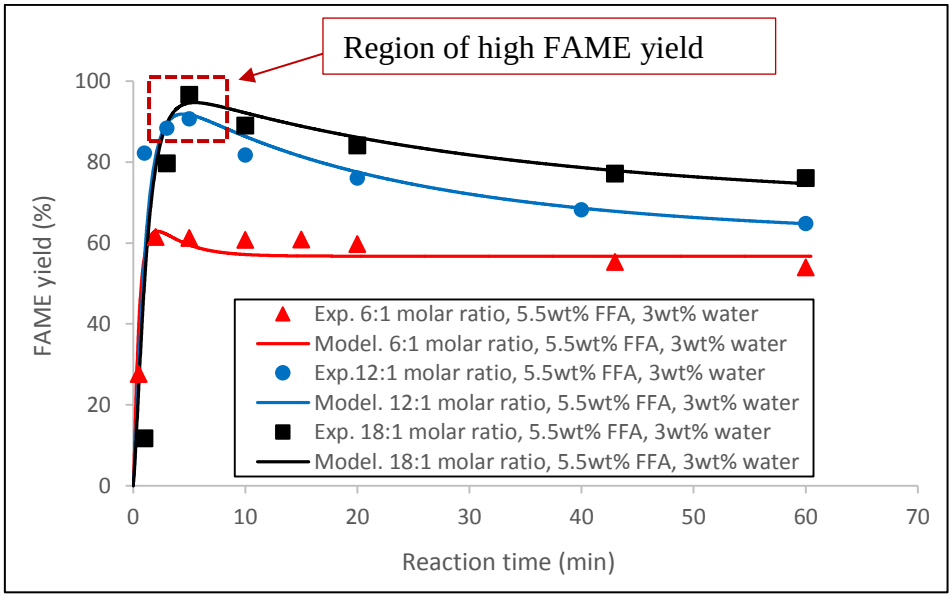

Fig. 7: Experimental and modelling results for transesterification at 60°C temperature, 3wt% $NaOCH_3$ and 600rpm stirrer mixing speed, using WCO containing 5.5wt% FFA and 3wt% water at 6:1, 12:1 and 18:1 methanol to WCO molar ratios.

A major finding in this study was that a single-step base-catalysed process can be tuned for rapid biodiesel production from waste cooking oil and other cheaply available triglyceride feedstock with up to 5.5wt% FFA and 3wt% water contents, to achieve FAME yields that meet biodiesel standards without any pre-treatment steps. This occurs within narrow operating conditions (2-5mins) at a molar ratio of 18:1 (Fig. 7). The use of base catalysts at these conditions would reduce the overall costs of biodiesel production

from cheap WCO feedstock that contains up to 5.5wt% FFA and 3wt% water contents, without any FFA esterification pre-treatment step.

It is known that using high methanol-to-oil molar ratio (18:1) leads to additional costs in the methanol recovery. It was reported that energy required for methanol recovery was 2390MJ/h (5.83MJ per kg of recovered methanol) for triglyceride (triolein) transesterification at 5250kg/h triolein throughput, 1h reaction time and 6:1 molar ratio of methanol to triolein in a conventional biodiesel process [52], compared to 11960MJ/h estimated for the 18:1 methanol-to-WCO used in this study. However, the conventional biodiesel process can only be used for refined vegetable oils or pre-treated waste cooking oil. The refined vegetable oils feedstock cost could contribute up to 60-70% of the total cost [31, 32] compared to less than 10% for energy cost [52]. Therefore, the total biodiesel production cost was reduced by over 60% when using direct WCO at 18:1 molar ratio. Although the reactor volume increased by around 1.40 times when 18:1 methanol-to-WCO molar ratio was used compared to the 6:1 molar ratio process, the reactor size would not increase at such due to a significant decrease in reaction time, i.e. from 1h to 5 mins. Hence, there will be a net reduction in the reactor volume by approximately 88%.

Pre-treatment of FFA in waste cooking oil is very energy intensive. Acid-catalysed FFA esterification requires a molar ratio of methanol to oil of about 20:1 [53], and this can be up to 40:1 molar ratio to achieve less than 1wt% FFA content in a triglyceride feedstock containing up to 5wt% FFA [54] over a long reaction time. One-step acid-catalysed transesterification of high FFA feedstock can be used, but this requires large excess of methanol [27] and the reaction is about 4000 times slower than base catalysts [16].

4.0 Conclusions

Process strategies for high FAME yield from waste cooking oil containing FFA of up to 5.5wt% and 3wt% water contents, was investigated using a single-step base-catalysed process. The reaction parameters were studied using both experimental and numerical simulations of the kinetic model (MATLAB). The kinetic model was used to identify conditions for achieving high FAME yields in the homogeneous $NaOCH_3$-catalysed transesterification at methanol to WCO molar ratios of 6:1 – 18:1, catalyst loadings in the range of 0.6wt% to 3wt%, FFA of 1.53wt% - 5.5wt%, 0.12wt% - 3wt% water content at reaction temperature of 60°C. FAME yields of 98.1 ± 2.0% at 12:1 and 98.0 ± 1.3% at 18:1 molar ratios were achieved using 3wt% catalyst for the WCO containing 1.53wt% FFA and 0.12wt% water, but only 92.8 ± 2.3 % FAME yield was obtained at 6:1 molar ratio. It was found that for high FFA and water contents in the WCO, methanol molar ratios of above 12:0 should be used to reduce loss in FAME yields due to saponification. At "high" FFA (5.5wt %) and water (3wt%) contents, an 18:1 molar ratio of methanol to WCO should be used to achieve ≥ 96.5% FAME conversion. The conditions identified in this study could be applied in biodiesel production from WCO and other cheap triglyceride feedstocks with high FFA and water contents using the one-step homogeneous alkali-catalysed process.

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